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(21) International Application Number: PCT/US91/06298 (22) International Filing Date: 9 September 1991 (09.09.91) (30) Priority data: 580,526 11 September 1990 (11.09.90) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor: OSTAPCHENKO, George, Joseph ; 202 Sadler Lane, Wilmington, DE 19803 (US). (74) Agents: KRUKIEL, Charles, E. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MN, MR (OAPI patent), MW, NL (European patent), NO, PL, RO, SD, SE (European patent), SN (OAPI patent), SU*, TD (OAPI patent), TG (OAPI patent). Published <i>With international search report.</i>
(54) Title: FILMS CONTAINING POLYHYDROXY ACIDS (57) Abstract The invention relates to films of blends of polyhydroxy acid and other compatible thermoplastic polymers, and their production by melt processing the materials to obtain uniform composition, and forming the composition into a film of thickness from 0.01 to 2 mm. Such films are useful for conventional film uses where the film is to be discarded into the environment after usage.		

+ DESIGNATIONS OF "SU"

Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

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TITLE

FILMS CONTAINING POLYHYDROXY ACIDS

5 BACKGROUND OF THE INVENTION

 This invention relates to certain films and
 their preparation, which films comprise a major
 component of polyhydroxy acid (PHA) and a minor amount
 of one or more other compatible thermoplastic poly-
10 mers.

 High molecular weight polymers of hydroxy
 acids and cyclic dimer products of esterification, of
 2-hydroxy acids, particularly glycolic acid and lactic
 acid, are well known to be degradable, and are found
15 useful for disposable packaging that will substan-
 tially and readily deteriorate to harmless by-products
 under conditions existing in the natural environment.
 It is desirable for packaging material to possess
 additional beneficial physical properties including
20 optical clarity, tensile strength, elasticity, resis-
 tance to puncture and, optionally, to be shrinkable.
 Shrinkable films are useful for "shrink-wrap" packag-
 ing. Shrink-wrapping is the process by which a film
 structure placed around an object contracts to provid
25 a tight, protective, self-sealing container, upon
 application of convective or radiant heat. In order
 to make polyhydroxy acid films shrinkable, they must
 be oriented by mechanical stretching procedures.

 Many high molecular weight polyhydroxy acids
30 of commercial significance contain large proportions
 of specific asymmetrical carbon atoms and may be,
 therefore, appreciably crystalline and brittle. Such
 polymers are less able to withstand demanding
 film-forming and orientation processes without
35 excessive film breakage causing low yield and
 productivity and films produced from them can become

brittle on aging. A method of making polyhydroxy acid film pliable is to plasticize it by incorporating large amounts of monomeric and low molecular weight oligomeric 2-hydroxy acid species. However, such plasticized polyhydroxy acid compositions can be difficult to extrude into films because they stick to the film-making equipment, produce films of non-uniform thickness and the plasticizer often fouls the equipment. When successfully processed to film form, significantly plasticized polyhydroxy acid compositions, by themselves, have glass transition temperatures, T_g , which are near ambient temperatures and may not be stable under storage conditions found in warm climates. In addition, they may not have appropriate rate of degradation to maintain structural integrity for the intended useful life of the package.

Schneider discloses in U.S. 2,703,316 the manufacture of films from lactic acid, but does not disclose blends with other polymers.

Encyclopedia of Polymer Science and Engineering, Mark et al., 1987, Vol. 3, pp. 758-775 and Vol. 12, pp. 417-424 describe a variety of polymer blends, the morphology thereof, and improved selected properties that can be tailored into polymer blends. Neither of these references contain disclosures of polyhydroxyacid blends or the property of degradability.

It is desirable to provide significantly degradable compositions that may be processed economically, and with high yield, into optically clear, robust film for commercially useful packaging and other applications, which films may have a balance of physical properties that can be tailored for particular uses.

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SUMMARY OF THE INVENTION

According to the present invention, there is now provided a process for making polymer films comprising:

5 melt processing the polymeric materials while subjecting the melt to sufficient mechanical agitation to obtain a uniform composition and thereafter forming a film, the polymer content of which comprises:

10 (a) from 55 to 90 wt% polyhydroxy acid polymer, and

(b) from 10 to about 45% of one or more compatible thermoplastic polymers other than those of (a).

There is also provided processes for making 15 shrinkable films, and non-shrinkable films having shrinkage values less than 5% at 100°C.

There are further provided articles made by the foregoing processes.

20 DETAILED DESCRIPTION OF THE INVENTION

The significant degradability of the films produced by this invention is achieved by use of polyhydroxy acids. "Polyhydroxy acids" as used herein means polymers containing at least one hydroxy acid 25 unit selected from among:

- (i) $[O(CR'R'')_nCO]_p$
- (ii) $(OCR'R''COOCR'P''CO)_q$
- (iii) $(OCR'R''CR'R''OCR'R''CO)_r$
- (iv) $(OCR'R''CR'R''ZCR'R''CR'R''CO)_s$
- 30 (v) copolymers of (i)-(iv) with non-hydroxy acid comonomers

wherein n is 2, 4 or 5; p, q, r and s are integers, the total of which may range from about 350 to 5,000; R' and R'' are independently hydrogen, hydrocarbyl 35 containing 1 to 12 carbon atoms, or substituted hydrocarbyl containing 1 to 12 carbon atoms, and Z is

oxygen, sulphur, NR' or PR'. The values of p, q, r and s are selected to impart degree of crystallinity and crystallization rates appropriate to the degree of orientation and the rate of degradation of the film desired.

Examples of non-hydroxy acid comonomers include those capable of condensation polymerization with lactide or lactic acid, i.e., lactones such as dodecanolactone, lactams and amino acids. For a more complete list see U.S. 4,800,219 at column 9, line 27.

Polyhydroxy acids of this invention have molecular weights at least high enough to provide sufficient viscosity and strength to form sustainable film from the blended polymer melt. For the PHA, weight average molecular weights from about 20,000 to about 600,000, and preferably at least about 50,000 and more preferably from about 150,000 to about 450,000, are effective in this invention. If the molecular weight is too high, excessive degradation occurs at the temperatures required to melt process the compositions.

Preferred polyhydroxy acids of this invention are those wherein 55-99 mol% of the PHA is composed of hydroxy acid units (i) wherein R' is hydrogen and R'' is the methyl radical, and having 80-97 mol% of asymmetric carbon atoms R- configuration and 3-20 mol% S- configuration; and wherein 1-45 mol% is composed of either hydroxy acid unit (i) of such asymmetric carbon content that the total R- or S- configuration do not exceed 97 mol% of asymmetric carbon atoms, or any hydroxy acid units (ii) to (iv) or suitable non-hydroxy acid comonomers.

Explanation of these preferred polyhydroxy acids is effectively achieved by example. A preferred polyhydroxy acid may, for example, contain 67 mol% hydroxy acid unit (i) in which 90 mol% of asymmetric

carbon atoms are S- configuration. The other 33% of polyhydroxy acid component might be completely composed of hydroxy acid unit (ii) or a suitable non-hydroxy acid comonomer. Or, the other 33% PHA might be additional hydroxy acid unit (i) but the fraction of asymmetric carbon atoms which are S- configuration in the 33% can be no greater than that which when added to the S- atoms of the 67% PHA component, does not raise the total S- atom content of the total PHA above 97 mol%.

In deciding the relative R- and S- contents, consideration must also be given to having a PHA that has a melting point close to the melting point of the other compatible polymer so as to promote maximum processibility and ultimate product properties. Thus, in some compositions the very high content of R- may be less desirable because of melting points substantially different than the other polymer.

The terms "R-" and "S-" refer to the standard nomenclature for identifying stereoisomer configurations of asymmetrical carbon. The percentages of R- and S- carbons indicated herein refer only to fractions of asymmetrical carbon atoms in the polymer chains and not to total carbon atoms in the polymer chains. Asymmetrical carbon atoms are those having no less than four different substituent radical groups attached to them.

The preferred compositions have narrow ranges of selected asymmetrical carbon atoms because polymers containing more equal fractions of R- and S- carbon atoms demonstrate accelerated degradation by hydrolysis, produce films adjacent layers of which often adhere to each other and which are prone to degradation during processing to form film.

Also, films made outside these ranges may be hazy and/or brittle. For example, polymer films

having fractions above the 97% S- carbon atom range are substantially crystalline after hot processing, such as in film production. Crystallinity is detrimental to film-forming capability, to optical clarity of films formed from crystalline polymers and to the ability to successfully orient films formed by stretching if desired. Crystalline polymer films are also more brittle than amorphous polymer films. A method for reducing the negative effects of highly crystalline polymer on film properties is to slightly plasticize the polymer by having monomeric or low molecular weight cyclic or oligomeric species dispersed within the polymer matrix.

It has been found that excessive concentration of plasticizers in polyhydroxy acids is undesirable. It produces films of uneven thickness. Where films are made by casting onto drums, excessive plasticizer may separate from the film, stick to and foul the drum, or may cause the film to stick to the drum. Thus, it has been found necessary to use polymer containing a minimal amount of plasticizer. The amount of plasticizers that can be included in the films of this invention is from about 0.10 to about 8 wt%, and preferably from about 0.2 to 6 wt% of the PHA content. A highly preferable composition range is from about 0.2 to 0.4 wt% plasticizer. These plasticizer levels are based upon the concentrations of the polyhydroxy acid and plasticizer in the feedstock to the film production process and not necessarily to the concentrations of the plasticizer in the film produced from compositions of this invention. Plasticizer content may be determined by analysis methods taught in Journal of Applied Polymer Science, Kohn, Van den Berg, Van de Ridder and Feyen, volume 29, pages 4265-4277 (1984). When necessary to

reduce the concentration of plasticizers in a plasticizer-rich composition, a devolatilizing extruder can be used either as a separate step or during film extrusion.

5 Non-polyhydroxy thermoplastic compatible polymers are those which are sufficiently compatible with PHA to produce biaxially oriented films having clarity that does not obscure or distort graphics on objects which have been wrapped by the biaxially
10 oriented film or which have been packaged in heat set, non-shrinkable film. Compatible polymers are characterized as having a sufficient number and distribution of hydrophilic groups selected from among hydroxy, ester, amide, ether carboxyl, ionic carboxy-
15 late and urethane. Preferred non-polyhydroxy polymers of this invention include polyesters, copolyetheresters, polyurethanes, ethylene/vinyl alcohol copolymers, copolyamideetheresters, ethylene/vinyl ester copolymers, copolyamideetheresters, ethylene/vinyl
20 ester copolymers and terpolymers, ethylene/vinyl acid and terpolymers and their metal salts, ethylene/carbon monoxide copolymers and copolyetherimidesters. Particularly preferred are the low molecular weight polyesters that have a high degree of degradability.

25 Shrinkage value is an indicator of film shrinkage performance. It is determined by cutting a 10 cm by 10 cm square sample from oriented film with edges of the sample parallel to machine and transverse film directions; immersing the sample in boiling water
30 for 1 minute; measuring and averaging the length and width of the boiled film; and calculating percent shrinkage value by subtracting the average boiled film length and width from 10, then multiplying the difference by 10. For example, assuming that the
35 average of length and width dimensions of a boiled

film sample is 6 cm, film shrinkage value is calculated as (10-6) times 10, r 40%.

It has been found that a particularly suitable compatible non-polyhydr xy acid for the purpose of this invention is a copolyetherester, which may be a copolyetherester elastomer commercially available from E. I. du Pont de Nemours & Company under the trademark "HYTREL". This copolyetherester elastomer consists essentially of a multiplicity of recurring intralinear long chain and short chain ester units connected head-to-tail through ester linkages, said long chain units being represented by the formula



and short chain ester units being represented by the formula



where G is a divalent radical remaining after the removal of terminal hydroxyl groups from a poly(alkylene oxide) glycol having an average molecular weight of 400 to 3500 and a ratio of the number of alkylene oxide carbon to oxygen atoms of 2 to 4.3, preferably 2.5 to 3.5; R' and R'' are divalent radicals remaining after removal of carboxyl groups from a dicarboxylic acid having a molecular weight less than 300; and D is a divalent radical remaining after the removal of hydroxyl groups from a diol having a molecular weight less than about 250. Said copolyetherester has from about 25 to 50 weight percent of short-chain ester units (V).

A particularly suitable copolyetherester of this type is one which contains about 25 weight percent of repeating units (IV) derived from 1,4-

butylene terephthalate and 75 weight percent of repeating units (V) derived from poly(tetramethylene ether) glycol terephthalate. The poly(tetramethylene ether) glycol used to make the copolyetherester has a
5 molecular weight of about 2000. This material is designated Copolyetherester A.

Another class of suitable non-polylactate polymers are ethylene/vinyl alcohol copolymers containing less than 50 mole % ethylene.

10 The term "degradable" as used here with respect to the polyhydroxy acids means that the degradable polyhydroxy acid portion of the material is biodegradable and, more importantly, degradable by hydrolysis. The degradation rate is consistent with
15 its intended usage, i.e., the product does not degrade significantly in normal storage and usage, but will degrade in a reasonable time, after discarding. The hydrolysis degradation of a polymer can be tailored readily to meet the requirements of use and disposal
20 of the film. It depends primarily on the nature of groups in the chains. Process conditions such as moisture, pH, temperature, ion strength, sunlight, enzymes, polymer crystallinity and hydrophilicity of the polymer affect degradation of the polymer, as is
25 well known.

Rate of degradation of polyhydroxy polymers can be too great for many typical packaging applications (i.e., the packaging film will deteriorate
30 excessively in less time than the expected shelf-life of the package, which includes the warehousing time of the packaging film between its production and application to the product). The reduced tensile strength of the film caused by the deterioration could result in film ruptures while being processed on shrink-wrap
35 machinery and would be unacceptable for commercial packaging applications. Also, the amount of shrinkage

or the resilience of the films may be inappropriate for particular uses. These deficiencies can be controlled by incorporating a non-polyhydroxy polymer in the polymer composition.

5 "Compatible polymer" as used herein means a non-PHA polymer that will blend with the PHA component sufficiently homogeneously as not to exhibit gross symptoms of polymer segregation. A non-PHA polymer/PHA polymer blend that is heterogeneous on a
10 microscopic level is considered incompatible (see Mack et al., Vol. 3, p. 759).

"Hazy" products, outside the scope of this invention, have impaired transparency caused by the exuding of low molecular weight plasticizer to the
15 surfaces of the films, high crystalline content of the starting PLA polymer, or inadequate compatibility or lack of microhomogeneous blending of the polymer blend.

Compositions of this invention are formed into films of uniform thickness from about 0.01 to 2
20 mm. Film forming may be accomplished by melt extrusion and sheet casting, blow molding, precipitation from solvent or other means well known to produce films from polymers. If desired, films thus formed may be fed directly to orientation
25 equipment or wound on spools or otherwise conveniently collected for storage and subsequent processing and use. These films normally have a tensile strength of 70-150 MPa and elongation at break of 50-90%.

Films useful in shrink-wrap packaging
30 applications may be prepared from many of the blends of this invention by biaxially orienting the films. Biaxially orienting means to stretch the film in the direction which it travels, called the machine direction (MD), and in the direction 90 degrees to the
35 machine direction in the plane of the film, known as the transverse or circumferential direction (TD),

thereby extending the film to at least two times its initial MD and TD direction dimensions, while heating and maintaining film temperature above the polyhydroxyacid glass transition temperature of the PHA below the melting temperature of all polymer components of the film, normally at least 5% below the melting point. Biaxial orienting of this invention includes all conventional techniques including simultaneous MD and TD stretching, sequential stretching, and tube blowing.

The polyhydroxyacid glass transition temperature is measured by differential scanning calorimetry (DSC). It decreases with increasing plasticizer content and is about 60°C for a composition containing 0.28 wt% plasticizer but only 40°C for a composition containing 20 wt% plasticizer. High plasticizer concentrations have been found unacceptable because the glass transition temperatures produced therefrom are too near temperatures encountered during storage and transport in warm climate regions.

Biaxially oriented films can be made non-shrinkable by heat-setting. Heat-setting is achieved by subjecting the oriented polymeric film to a temperature above the polyhydroxyacid glass transition temperature but well below its melting temperature while maintaining the film under restraint. The duration of heat-setting found effective is from about 1 to 120 seconds and preferably from about 1 to 80 seconds. "Non-shrinkable" products of this invention are defined as films that will not shrink more than 5% when immersed in boiling water for 1 minute. Non-shrinkable degradable films are useful for production of microwave-cookable food packaging, trash bags and waste container liners, for example.

EXAMPLES

This invention is now illustrated by representative examples of certain preferred embodiments thereof, where all parts, proportions, and percentages are by weight, unless otherwise indicated. All units of weight and measure other than SI units have been converted to SI units.

EXAMPLE 1

A blend consisting of 65% of an 85-95% S-/5-15% R- optically active carbon content polylactide having about 6% plasticizer and molecular weight of about 350,000, and 35% of Copolyetherester A, is extruded into a film of 0.2 mm thickness. It is biaxially oriented by stretching 3X in the MD and TD, at a temperature of ⁷⁵130°C to produce a film having shrinkage value in boiling water of 55%, a tensile strength of 73 MPa and an elongation at break of 58%.

EXAMPLE 2

A blend consisting of 70% of polylactide having about 95% S-/5% R- optically active carbons, molecular weight of about 200,000 and about 2% plasticizer as determined by lactide content analysis, and 30% of ethylene/vinyl alcohol copolymer with ethylene content of 44 mole %, is extruded into a 0.23 mm thick film.

The film is biaxially oriented as described in Example 1 to produce a film having a shrinkage value of 42% in boiling water, tensile strength of 150 MPa and elongations at break of 85%. The biaxially oriented film has excellent shrink-wrap capability and no film degradation is observed after aging 12 months at room temperature, indicating significant shelf life for this film.

EXAMPLE 3

Prior to heat-setting, a sample of the biaxially oriented film of Example 1 is wrapped around a 7.6 cm wide, 12.7 cm long, 0.64 cm high pad of paper and held in place with double-sided adhesive tape. The wrapped package is placed in a hot air convection oven at 100°C for one minute. The film shrinks uniformly around the pad and is optically clear and glossy.

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WHAT IS CLAIMED IS

1. A process for making polymer film comprising:

5 (I) melt processing compatible thermoplastic polymeric materials while subjecting the melt to sufficient mechanical agitation to obtain a uniform composition, the polymer content of which comprises:

10 (a) from 55 to 90 wt% polyhydroxyacid polymer containing at least one hydroxy acid unit selected from among:

(i) $[O(CR'R'')_nCO]_p$

(ii) $(OCR'R''COOCR'R''CO)_q$

(iii) $(OCR'R''CR'R''OCR'R''CO)_r$

15 (iv) $(OCR'R''CR'R''ZCR'R''CR'R''CO)_s$

(v) copolymers of (i)-(iv) with non-hydroxy acid comonomers

wherein n is 2, 4 or 5; p, q, r and s are integers, the total of which may range from about 350 to 5,000;

20 R' and R'' are independently selected from hydrogen, hydrocarbyl containing 1 to 12 carbon atoms, and substituted hydrocarbyl containing 1 to 12 carbon atoms, Z is oxygen, sulphur, NR' or PR'; and

(b) from 10 to about 45% of one or more
25 compatible thermoplastic polymers other than those of (a); and

(II) forming the composition into a film of uniform thickness from about 0.01 to 2 mm.

30 2. The process of Claim 1, wherein the film is stretched to greater than two times its initial machine direction and transverse direction dimensions at a temperature above the polyhydroxyacid glass transition temperature and at least 5°C below the
35 melting temperature of the composition.

3. A process of Claim 1, wherein polyhydroxyacid component has weight average molecular weight from about 20,000 to 600,000.

5 4. A process of Claim 1, wherein polyhydroxy acid component has weight average molecular weight from about 150,000 to 450,000.

5. A process of Claim 3, wherein the number
10 of moles hydroxy acid units (i) is at least 80% of the total moles of hydroxy acid units.

6. A process of Claim 3, wherein the number
15 of moles hydroxy acid units (i) is at least 85% of the total moles of hydroxy acid units.

7. A process of Claim 5, wherein R' in
hydroxy acid units (i) is hydrogen and R'' in hydroxy
acid units (i) is the methyl radical.

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8. A process of Claim 5, wherein R' in
hydroxy acid units (i) is hydrogen and R'' in hydroxy
acid units (i) is the methyl radical.

25 9. A process of Claim 6, wherein asymmetric carbon atoms in the polymer chain are substantially exclusively R- or exclusively S- configurations.

10. A process of Claim 7, wherein asymmetric
30 carbon atoms in the polymer chain are substantially exclusively R- or exclusively S- configurations.

11. A process of Claim 3, wherein the
polyhydroxy acid component comprises
35 a major component of 55-99 mol% hydroxy acid units (i) wherein R' is hydrogen and R'' is the

methyl radical and having 80-97 mol% of asymmetric carbon atoms selected from R- configuration and S- configuration, and

5 a minor component of 1-45 mol% further comprising at least one of

(a) hydroxy unit (i) of asymmetric carbon content such that the total of a single type of asymmetric carbon atoms in major and minor components do not exceed 97 mol% of the total asymmetric carbon atoms, and

(b) hydroxy units selected from those of. formutal (ii), (iii), (iv) and suitable non-hydroxy acid comonomer.

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12. A process of Claim 10, wherein the total content of a single asymmetric carbonation of the polyhydroxy acid is 85-96 mol% of the total asymmetrical carbon atoms.

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13. A process of Claim 3, wherein the polyhydroxy acid component comprises hydroxy acid units (i) wherein R' is hydrogen and R'' is the methyl radical and having 80-97 mol% of asymmetric carbon atoms selected from R- configuration and S- configuration.

14. A process of Claim 3, wherein the polyhydroxy acid component comprises hydroxy acid units (i) wherein R' is hydrogen and R'' is the methyl radical and having mol% of asymmetric carbon atoms selected from 85-95% R- configuration plus 4-15 S- configuration, and 85-96 S- configuration plus 4-15 R- configuration.

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15. A process of Claim 11, wherein the film contains from 0.2 to 6 wt% plasticizer.

16. A process of Claim 11, where in the film contains from 0.2 to 0.4 wt% plasticizer.

17. A process of Claim 15, wherein the concentration of plasticizer in the polyhydroxy acid composition is controlled by polymerizing the polyhydroxy acid from a mixture of lactides and acids producing a plasticizer-containing product and wherein the plasticizer concentration is reduced to final concentration by devolatilization in the melt processing apparatus.

18. A film made by the process of Claim 1.

19. A film of Claim 2, having shrinkage value greater than 40% at 100°C.

20. Polymer films comprising:

(I) from 55 to 90 wt% polyhydroxyacid polymer containing at least one hydroxy acid unit selected from among:

- (i) $[O(CR'R'')_nCO]_p$
- (ii) $(OCR'R''COOCR'R''CO)_q$
- (iii) $(OCR'R''CR'R''OCR'R''CO)_r$
- (iv) $(OCR'R''CR'R''ZCR'R''CR'R''CO)_s$
- (v) copolymers of (i)-(iv) with non-hydroxy acid comonomers

wherein n is 2, 4 or 5; p, q, r and s are integers, the total of which equals 350 to 5,000; R' and R'' are independently selected from hydrogen, hydrocarbyl containing 1 to 12 carbon atoms, and substituted hydrocarbyl containing 1 to 12 carbon atoms; and Z is selected from oxygen, sulphur, NR' or PR'; and

(II) from 10 to about 45% of compatible thermo-plastic polymer other than those of (i) to (v).

21. Film of Claim 20, wherein polyhydroxy acid component has weight average molecular weight from about 150,000 to 450,000.

5 22. Film of Claim 21 wherein the polyhydroxy acid component comprises hydroxy acid units (i) wherein R' is hydrogen and R'' is the methyl radical and having 85-96 mol% of asymmetric carbon atoms selected from R- configuration and S- configuration.

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 23. Film of Claim 22, wherein the polyhydroxy acid composition consists of 94 to 99.8 wt% polyhydroxy acid component and from 0.2 to 6 wt% plasticizer.

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 24. Film of Claim 22, wherein the polyhydroxy acid composition consists of 99.6 to 99.8 wt% polyhydroxy acid component and from 0.2 to 0.4 wt% plasticizer.

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 25. Non-shrinkable films of Claim 21, having a shrinkage value less than 5% at 100°C.

25 26. Film of Claim 20 wherein the compatible polymer comprises a copolyetherester.

 27. Film of Claim 20 wherein the compatible polymer comprises ethylene/vinyl alcohol.

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 28. Film of Claim 20 wherein the compatible polymer comprises a polyolefin.

 29. Film of Claim 21 wherein the compatible polymer comprises a low molecular weight polyester.

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30. Film of Claim 20 having tensile strength of 70 to 150 MPa and elongation at break of 50-90%.

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INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/06298

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC IPC (5): C08L 67/04 U.S. CL: 525/411, 437; 524/539											
II. FIELDS SEARCHED <table style="width: 100%; border: none;"> <tr> <td style="width: 30%; border: none;"></td> <td style="border: none; text-align: center;">Minimum Documentation Searched ⁷</td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;">Classification System</td> <td style="border: 1px solid black; padding: 5px;">Classification Symbols</td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;">U.S.</td> <td style="border: 1px solid black; padding: 5px;">525/411, 437; 524/539</td> </tr> </table> <p style="text-align: center; font-size: small;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *</p>				Minimum Documentation Searched ⁷	Classification System	Classification Symbols	U.S.	525/411, 437; 524/539			
	Minimum Documentation Searched ⁷										
Classification System	Classification Symbols										
U.S.	525/411, 437; 524/539										
III. DOCUMENTS CONSIDERED TO BE RELEVANT * <table style="width: 100%; border: none;"> <tr> <th style="width: 10%; border: 1px solid black; padding: 5px;">Category *</th> <th style="width: 70%; border: 1px solid black; padding: 5px;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%; border: 1px solid black; padding: 5px;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="border: 1px solid black; padding: 5px;">US, A, 4,661,530 (GOGOLEWSKI) 28 APRIL 1987 See entire document.</td> <td style="border: 1px solid black; vertical-align: top; padding: 5px;">20, 21, 25, 30</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="border: 1px solid black; padding: 5px;">US, A, 3,892,821 (KOLESKE) 01 JULY 1975 See entire document.</td> <td style="border: 1px solid black; vertical-align: top; padding: 5px;">1-16, 18-25, 30</td> </tr> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	US, A, 4,661,530 (GOGOLEWSKI) 28 APRIL 1987 See entire document.	20, 21, 25, 30	X	US, A, 3,892,821 (KOLESKE) 01 JULY 1975 See entire document.	1-16, 18-25, 30
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X	US, A, 4,661,530 (GOGOLEWSKI) 28 APRIL 1987 See entire document.	20, 21, 25, 30									
X	US, A, 3,892,821 (KOLESKE) 01 JULY 1975 See entire document.	1-16, 18-25, 30									
<div style="display: flex; justify-content: space-between; font-size: x-small;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>											
IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> Date of the Actual Completion of the International Search <div style="text-align: center; font-size: large;">19 NOVEMBER 1991</div> </td> <td style="width: 50%; border: none; vertical-align: top;"> Date of Mailing of this International Search Report <div style="text-align: center; font-size: x-large;">16 DEC 1991</div> </td> </tr> <tr> <td style="border: none; vertical-align: top;"> International Searching Authority <div style="text-align: center;">ISA/US</div> </td> <td style="border: none; vertical-align: top;"> Signature of Authorized Officer <div style="text-align: center;"> Patricia Short <i>Patricia Short</i> </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center; font-size: large;">19 NOVEMBER 1991</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-size: x-large;">16 DEC 1991</div>	International Searching Authority <div style="text-align: center;">ISA/US</div>	Signature of Authorized Officer <div style="text-align: center;"> Patricia Short <i>Patricia Short</i> </div>					
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FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____ because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____ because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

3. ☐ Claim numbers _____ because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING²

This International Searching Authority found multiple inventions in this international application as follows:

see attachment.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

1-26, 30

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
☐ No protest accompanied the payment of additional search fees.

CONTINUATION FORM PCT/ISA210 PART VI OBSERVATIONS
WHERE UNITY OF INVENTION IS LACKING

The claims are drawn to a plurality of distinct species comprising film and process of making in which the compatible thermoplastic polymer is:

- | | |
|---------------------------|------------------------|
| I. copolyetherester | claims 1-26 and 30 |
| II. ethylene/vinylalcohol | claims 1-25, 27 and 30 |
| III. polyolefin | claims 1-25, 28 and 30 |
| IV. polyester | claims 1-25, 29 and 30 |
| V. polyurethane | claims 1-25, 30. |